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FINGERPRINT NEUTRALIZING COMPOUNDS

III - Investigation of Alcohols and Other Organic Solvents as Fingerprint Removers

Project Title: Development of Test Methods, Materials and Applications for Fingerprint Neutralizing Compounds

Project No.: TB5-8206A

Report No.: 3

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FINGERPRINT NEUTRALIZING COMPOUNDS

III - Investigation of Alcohols and Other Organic Solvents as Fingerprint Removers

Object

To investigate the fingerprint removing properties of various alcohols and other organic solvents (representative of Type B, U. S. Army Tentative Specification AXS-1719).

To study the effect of adding inhibitors or wetting agents to alcohol-water mixtures used for fingerprint removal.

To compare the speed of removal of various alcohol-water mixtures and alkylolamine soap formulations. (The latter are representative of Type A, U. S. Army Tentative Specification AXS-1719).

Summary

Several alcohols, alcohol-water mixtures and solutions of organic solvents were investigated to determine their efficiency as fingerprint removers.

Various isopropanol-water mixtures were investigated to determine the effect of added corrosion inhibitors or wetting agents on their efficiency as fingerprint removers.

Studies were conducted to determine the speed of removal which could be attained using alcohol-water mixtures and alkylolamine soap formulations prepared in this laboratory.

Conclusions

Of the alcohols tested, methanol was found to have the best fingerprint removal efficiency. This property decreased rapidly as the homologous series was ascended.

The other organic solvents tested ranged from poor to good as regards fingerprint removal.

The addition of small quantities of water was found to improve the removal action of some of the solvents, but in higher concentrations generally produced overall rusting.

The addition of corrosion inhibitors or wetting agents did not improve the removal action perceptibly. However, the inhibitors acted to prevent corrosion by the moisture and salt residues which might remain after treatment.

Type B compounds can be formulated which are less dangerous to use than methanol and which will apparently remove fingerprints in the space of a few seconds.

Currently procurable Type A compounds remove fingerprints more slowly and further development will be required to achieve speedier performance.

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Introduction

1. U. S. Army Tentative Specification AXS-1719 specifies two types of fingerprint remover compounds, namely:

Type A - a remover and temporary preservative

Type B - a remover only.

2. Because methyl alcohol, which has been widely used as a Type B fingerprint remover, has obvious drawbacks with respect to safety, it was felt that a less inflammable, less toxic material would be highly desirable. Therefore, this limited investigation was undertaken to survey the field of possible Type B compounds and to evaluate some of them.

3. There are two general classes of materials, besides methanol, which experience indicates would possibly meet the requirements for a Type B compound, namely:

(a) Mixtures of various alcohols and water with small percentages of corrosion inhibitors or wetting agents.

(b) Soluble oil or solubilized oil and water mixtures such as:

(1) Emulsion cleaners

(2) Dry cleaning soaps

(3) Emulsifiable soluble oils.

4. The successful use of methanol, in the past, led to the investigation of its homologues to determine their effectiveness as fingerprint removers. The investigation was then broadened to include representative compounds of the glycol-ethers, ketones and alkylolamine soap formulations.

5. One other consideration of utmost importance for fingerprint removers of either type is the speed with which they will remove the corrosive salt residues from the material being processed. As a result, considerable space in this report will be devoted to results obtained from speed of removal tests run with alcohol-water mixtures and alkylolamine soap formulations, both with and without additives.

6. It is also believed that this investigation will prove of academic interest in defining a property of the organic solvents employed.

Results and Discussion

Effectiveness of Removal by Organic Solvents.

7. The removal tests to be reported upon in succeeding paragraphs were all conducted in accordance with paragraph F-4e of the proposed specification which is included in a previous report(1) as Appendix 2. This empirical method consisted of printing previously polished and cleaned WD 1020 steel panels with one drop of the synthetic fingerprinting solution specified by Specification AXS-1719, the composition of which is analogous to human perspiration. The panel was immediately placed in a forced draft oven for 5 minutes at 250°F. for rapid drying of the print. After removal from the oven and cooling, the panel was ready for test. The solutions

(1) Eisler, S. L., "Fingerprint Neutralizing Compounds, II - Proposed Revisions to U. S. Army Tentative Specification AXS-1719 (RIA Lab. Report 48-558)".

and the treatment times employed were varied as designated in the individual tests reported later in this report. After treatment in these solutions the panels were air dried and then exposed for 18 hours in a 100% static humidity, obtained by partially filling a dessicator with distilled water, and maintained at 77° ± 2°F. The above method is empirical but provides a satisfactory and reasonably reproducible method of evaluating test solutions. The rating system employed is based upon a comparison of the intensity and area of rusting within the printed area with two limits designated 0% and 100%. 0% indicates complete intense rusting of the printed area or no removal, while 100% indicates the absence of rust and complete removal of the salt residues.

8. The range of the results of tests conducted using methanol and its homologues are presented in Table 1, and of tests using other organic solvents in Table 2. The number of solvents investigated was limited because of the promise shown by various alcohol-water and acetone-water mixtures.

9. An analysis of the data presented in Tables 1 and 2 reveals the following salient facts:

(a) The degree of removal by the alcohols progressively decreased with an increase in the number of carbon atoms contained in the alcohol.

(b) In general, the addition of water to the various solvents increased the removal property. This was partially

masked when larger amounts of water were added, due to the general rusting over the entire panel. The overall rusting was found to be more intense when the test panel was in the solution for a longer length of time, indicating that this condition was due to the high proportion of water in the solution.

(c) The removal efficiency of methanol was not appreciably improved by the addition of small percentages of water.

(d) Isopropanol, of the alcohols, and the other organic solvents were not tested under the shorter treatment conditions since preliminary tests had shown that their removal properties were limited.

(e) Further consideration of the problem of water addition revealed that there was no definite pattern of behavior common to all of the solvents tested. This is in contrast to work done in the past to study the effect of water additions to alkylolamine soap formulations. For the latter, the degree of fingerprint removal increased as the percentage of water was increased and was limited only by the amount of water which could be added without producing an unstable solution.

(f) In all tests where comparisons are available, it will be noticed that agitation of the panel in the test solution produced a higher degree of removal than when the panels were not agitated, as would be expected.

(g) In regard to speed of removal, methanol was the only solvent tested which would remove all traces of salt residues in the comparatively short treatment time of 15 seconds. However, due to its toxicity and low flash point, the use of methanol as a fingerprint neutralizer is discouraged.

(h) The carbitol mixtures were quite effective as regards removal, but the extremely slow drying time and the subsequent overall rusting produced, makes their use impracticable.

(i) The acetone mixtures were also effective when higher water concentrations were used. However, the overall rusting produced on the panels proved a distinct disadvantage.

10. In the use of alcohol-water or other solvent-water mixtures containing relatively high percentages of water, it should be borne in mind that the retention of any water droplets on the material being processed, due to incomplete drying, might have a serious effect on the protection afforded by subsequently applied permanent rust preventives.

Effect of Added Inhibitors and Wetting Agents

11. The undesirability of using methanol as a possible Type B compound due to its toxicity prompted the investigation of other alcohol-water mixtures with additives to improve the degree and rapidity of removal of the corrosive salts and to eliminate the general rusting. The investigation was concentrated on isopropanol-water mixtures due to their ready

availability, higher flash point and low degree of toxicity.

12. The agents used were either inhibitors or wetting agents as it was believed the wetting agents might improve the detergency while an inhibitor would tend to prevent overall rusting due to the high water content. The inhibitors used were as follows:

(a) 0.2% Sodium Nitrite

(b) Naval Research Lab. Formula consisting of 0.3% borax, 0.3% sodium dihydrogen phosphate and 0.1% of the sodium salt of mercaptobenzothiazole(2)

The wetting agents employed were:

(a) 0.1% Nacconal NR

(b) 0.1% Triton NE

13. A preliminary investigation was conducted using a 60% isopropanol solution containing 0.2% of sodium nitrite. The panels were printed with the full strength fingerprinting solution and then treated by various methods in the test solution. A companion set of panels were run in an identical manner using the 60% isopropanol solution without inhibitor. The results of this test are pictured in Figure 1. The following points are to be noted:

(a) The intensity of the overall rusting produced in the uninhibited solution was proportional to the time of treatment. This was to be expected as the water content is very high and rusting would be intensified by longer exposure

(2) "The Development of the Hydrolube Non-Inflammable Hydraulic Fluids", NRL Report No. P-3020, April 1947.

in such a solution.

(b) The salt residues were apparently completely removed by agitation in the inhibited solution, but not when the immersion treatment was employed.

(c) All panels treated in the inhibited solution were free of salt residue corrosion and overall rusting.

14. The apparently excellent performance of the 60% isopropanol solution containing 0.2% sodium nitrite in the above test raised the question as to how rapidly this solution could remove the salt residues from the panel. Therefore, panels printed with 25%, 50% and 100% strengths of the fingerprinting solution and natural prints were treated in this solution by two methods, namely; a single dip and a 3-second agitation. All panels so treated showed no rust after 18 hours exposure in the 100% static humidity. There was some evidence of stain at the bottom of the panels given the single dip treatment which was possibly due to traces of salt residues in the water droplets which did not drain off the panel.

15. The results of the above two tests indicate that the inhibited isopropanol solution will prevent salt residue corrosion when a very short treatment time is employed. However, it remained to be proven whether the salt residues were actually removed by the solution or whether the sodium nitrite in the solution acted merely to inhibit the corrosion which normally would develop due to the salts remaining on the panels. This will be considered further in paragraph 21.

16. The results of several further tests using various isopropanol solutions and additives are given in Table 3. The following comments may be made concerning these results:

(a) The detergents, which were used only in the solutions containing the lower percentages of water, had no perceptible effect upon the degree of removal.

(b) Both inhibitors used apparently improved the removal efficiency materially. In fact, solutions which would have failed the specification requirement without the inhibitor, passed the requirement upon addition of the inhibitor.

(c) The solutions containing sodium nitrite gave excellent results in every instance.

(d) The solutions containing the NRL formula left a slight whitish stain on the panel which was not believed to be harmful.

17. The detergents were added to the solution which showed the poorest removal efficiency as it was felt their action, if any, would be to improve the removal of the corrosive salts. On the other hand, the inhibitors were added only to solutions which produced overall rusting as it was believed their action would tend to reduce this condition.

18. In order to evaluate the inhibitors used above more accurately, another series of tests was performed in which the treatment time was greatly reduced. The results of this test are presented in Table 4. It will be noted that:

(a) The uninhibited solution effected no removal at all.

(b) The solutions containing the NRL formulation proved to be greatly inferior to the sodium nitrite inhibited solutions as regards the degree of apparent removal.

(c) The panels given the longer treatment of 5 seconds agitation showed less corrosion due to the salt residues than the panels given only a single dip treatment.

(d) The light film or stain noted on the panels tested in the sodium nitrite inhibited solutions was not removable with chloroform but was not considered objectionable.

19. Since the use of sodium nitrite had proved so successful in apparently improving the removal quality of isopropanol-water mixtures it was decided to use it as an additive to some alkylolamine soap formulations, prepared at this Arsenal, which had not proved effective as removers when very short treatment times were employed.

20. The results of tests using formulations RIL #246 and RIL #247 with and without 0.2% of sodium nitrite are pictured in Figures 2 and 3. It may be noted that in every case the degree of apparent removal in the inhibited solution was greater than the corresponding test in the uninhibited solution. However, complete removal was not effected until a treatment of 60 seconds agitation in the inhibited solution was used.

21. The question raised in paragraph 15 as to whether the sodium nitrite acts to improve the detergent action or merely as an inhibitor was answered, at least for this type of formulation, by the tests described in paragraph 20. The test panels were examined after having been agitated in the inhibited and uninhibited test solutions. The remaining salt residues on companion panels appeared practically identical. This would seem to indicate that the sodium nitrite acts mainly to prevent rusting due to the salt residues and has little effect on the removal characteristics of the solution to which it is added. A similar test using inhibited and non-inhibited 60% isopropanol solutions gave the same results as outlined above.

Speed of Removal

22. The subject of speed of removal has been more or less covered in the two previous sections. However, a statement as to the importance of this problem seems appropriate at this time. Modern day assembly line production places considerable stress on speed and continuity of operation. Consequently, there is a tendency to disapprove of any operation requiring a considerable length of time. The present specification time of two minutes with constant agitation for removal of the fingerprint residues (for both types) seems unnecessarily long. However, the presently available commercial Type A products will not pass a more stringent test, so its retention in its present form is necessary.

23. In order to develop solutions capable of removing salt residues in as short a time as possible it is planned to formulate several such solutions in this laboratory. One such solution, prepared in this laboratory two years ago and designated RIL #245 was retested during this investigation with very encouraging results. The results of two tests using RIL #245 plus 40% of water are given in Table 5. It will be noted that in one case complete removal of the salt residues was obtained with only a single dip treatment. The only disadvantage to the use of this solution, which was not considered particularly objectionable, was that a light soap-like residue remained on the printed area after treatment. There was, however, no evidence of rust formation on the panel.

General Discussion

24. The advantages and disadvantages of each of the three general classes tested are as follows:

(a) Methanol is a very good remover, comparatively inexpensive and readily available. Its use is not desirable due to its low flash point and toxicity.

(b) The alcohol-water mixtures are also good removers, even less expensive than methanol, if higher percentages of water are used, and also readily available. Their disadvantages are their comparatively low flash point, corrosiveness, slow drying due to the high water content and incompatibility of

persisting moisture residues with subsequently used final rust preventives.

(c) The soluble oil or solublized oil and water mixtures, although more expensive than the above two classes, minimize the objections attributed to free moisture content by reason of solubilization. This class of compounds need not have the disadvantage of low flash points or toxicity.

25. The solublizied oil formulations, as represented by Formulations RIL #245 and RIL #246 could very easily be converted to effective Type B compounds by reducing the quantity of rust inhibitor in the formulation. It is believed this type of formulation can be improved to the point where removal can be effected in a much shorter time, as evidenced by the results obtained with Formulation RIL #245. These, however, may leave a light soap-like residue on the panels which is not considered deleterious.

26. The efficiency of the alcohol-water and other solvent water mixtures can be materially improved by the addition of corrosion inhibitors. However, it is not possible to predict the length of time that the action of the inhibitors would remain effective.

27. Referring to a previously cited report(1) the need for Type B compounds was questioned if satisfactory Type A compounds are available. It was mentioned that there were two plausible reasons for the retention of a Type B compound in the specification, namely:

(a) Possible lower cost

(b) The possibility of incompatibility of Type A compounds with subsequently applied permanent rust preventives. The question of cost is believed to be significant and should not be summarily dismissed. As regards the compatibility of the Type A compounds with permanent rust preventives, tests are now in progress to answer this question and these will be reported subsequently. The results to date indicate that no difficulty need be anticipated.

28. In line with the discussion of the preceeding paragraphs, no further work on the alcohols and other solvents as fingerprint removers is planned at this time.

29. The future work on this project will deal mainly with the following two problems:

(a) Practical considerations involved in shop use of these materials

(b) Formulation of solutions which will be less corrosive and which will effect speedier removal of fingerprint residues.

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Tests by: Stanley L. Eisler
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Supervised by: Harry L. Faigen

Reviewed by: Gerald O. Inman

Approved by: H. A. Curtis

Prior Reports on this Project

RIA Lab. Report 48-238, "Fingerprint Neutralizing Compounds, I - Statement of Problem and Investigation of Synthetic Fingerprint Solutions".

RIA Lab. Report 48-558, "Fingerprint Neutralizing Compounds, II - Proposed Revisions to U. S. Army Tentative Specification AXS-1719".

Table 1

Average Percent Effectiveness of Removal by Alcohols

Treatment / Alcohol	15 Sec. Agitation	120 Sec. Agitation	120 Sec. Immersion	600 Sec. Immersion
100% Methanol	99-100	99-100	97-99	95-100
95% "	100	100	95	96-100
93% "	100	100	99-100	90-98
90% "	98-99	100	85	80
*80% "	96-100	95-100	80-100	30-50
*60% "	90-100	90-100	85	30
95% Ethanol	80-90	90-99	50-60	30-40
*80% "	95-97	90-97	30-50	10-30
*70% "	96-100	90-100	20-30	0
*60% "	90-92	100	50	0
100% Isopropanol		0		0
*80% "		90		0
*70% "		85-95		0
*60% "		85-90		0
100% Butanol		0		
90% "		0		
*80% "		0		
100% Pentasol (mixed isomeric amyl alcohols)		0		
90% " " "		0		

*Indicates general overall rusting.

Table 2

Average Percent Effectiveness of Removal by Other Organic Solvents

Treatment Solvent	15 Sec. Agitation	120 Sec. Agitation	120 Sec. Immersion	600 Sec. Immersion
100% Ethyl Cellusolve	------	60-80	------	60-80
80% " "	------	95-100	------	30-50
100% Carbitol	90	95-100	95	90-92
** 80% "	100	99-100	100	100
100% Acetone	------	0	------	0
80% "	50-60	100	------	50
*60% "	90	97-100	------	30

*indicates general overall rusting.

**indicates general overall rusting, printed area not discernible.

Table 3

Fingerprint Removal Tests

Isopropanol-Water Solutions with Additives
Treatment: 120 Sec. agitation

% Alcohol	Additive	% Effectiveness of Removal
100	None	0
"	0.1% Nacconal	0
"	0.1% Triton NE	0
90	None	0
"	0.1% Nacconal	0
"	0.1% Triton NE	0
80	None	90
"	0.2% $NaNO_2$	100
"	NRL Formula	95 Stained
70	None	85
"	0.2% $NaNO_2$	100
"	NRL Formula	100 Stained
60	None	85-90
"	0.2% $NaNO_2$	100
"	NRL Formula	100 Stained

Table 4

Fingerprint Removal Test
Isopropanol Solutions with Inhibitors

% Alcohol	Additive	% Effectiveness of Removal 5 Sec. Agitation	Single Dip
80%	None	0	0
	0.2% $NaNO_2$	97 (stain)	93 (stain)
	N.R.L.	0	0
70%	None	0	0
	0.2% $NaNO_2$	100 (lt. stain)	95 (lt. film)
	N.R.L.	30	0
60%	None	0	0
	0.2% $NaNO_2$	95 (lt. film)	93 (lt. film)
	N.R.L.	60	20

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Date: 8 December 1948

(10) S. L. Eisler

Table 5

Fingerprint Removal Test

Formulation RIL #245 plus 40% H_2O

Treatment	% Effectiveness of Removal Test (A)	Test (B)
Single Dip	90%	100%
3 Sec. Agitation	95%	100%
5 Sec. Agitation	100%	98-99%
10 Sec. Agitation	85%	98-99%
15 Sec. Agitation	100%	100%
5 Sec. Soak	97%	98-99%
15 Sec. Soak	100%	95%
30 Sec. Soak	100%	99%

Table 1

Average Percent Effectiveness of Removal by Alcohols

Treatment Alcohol	15 Sec. Agitation	120 Sec. Agitation	120 Sec. Immersion	600 Sec. Immersion
100% Methanol	99-100	99-100	97-99	95-100
95% "	100	100	95	96-100
93% "	100	100	99-100	90-98
90% "	98-99	100	85	80
*80% "	96-100	95-100	80-100	30-50
*60% "	90-100	90-100	85	30
95% Ethanol	80-90	90-99	50-60	30-40
*80% "	95-97	90-97	30-50	10-30
*70% "	96-100	90-100	20-30	0
*60% "	90-92	100	50	0
100% Isopropanol		0		0
*80% "		90		0
*70% "		85-95		0
*60% "		85-90		0
100% Butanol		0		
90% "		0		
*80% "		0		
100% Pentasol (mixed isomeric amyl alcohols)		0		
90% " " "		0		

*Indicates general overall rusting.

Table 2

Average Percent Effectiveness of Removal by Other Organic Solvents

Treatment Solvent	15 Sec. Agitation	120 Sec. Agitation	120 Sec. Immersion	600 Sec. Immersion
100% Ethyl Cellusolve	------	60-80	------	60-80
80% " "	------	95-100	------	30-50
100% Carbitol	90	95-100	95	90-92
** 80% "	100	99-100	100	100
100% Acetone	------	0	------	0
80% "	50-60	100	------	50
*60% "	90	97-100	------	30

*indicates general overall rusting.

**indicates general overall rusting, printed area not discernible.

Table 3

Fingerprint Removal Tests

Isopropanol-Water Solutions with Additives
Treatment: 120 Sec. agitation

% Alcohol	Additive	% Effectiveness of Removal
100	None	0
"	0.1% Nacconal	0
"	0.1% Triton NE	0
90	None	0
"	0.1% Nacconal	0
"	0.1% Triton NE	0
80	None	90
"	0.2% $NaNO_2$	100
"	NRL Formula	95 Stained
70	None	85
"	0.2% $NaNO_2$	100
"	NRL Formula	100 Stained
60	None	85-90
"	0.2% $NaNO_2$	100
"	NRL Formula	100 Stained

Table 4

Fingerprint Removal Test
Isopropanol Solutions with Inhibitors

% Alcohol	Additive	% Effectiveness of Removal 5 Sec. Agitation	Single Dip
80%	None	0	0
	0.2% $NaNO_2$	97 (stain)	93 (stain)
	N.R.L.	0	0
70%	None	0	0
	0.2% $NaNO_2$	100 (lt. stain)	95 (lt. film)
	N.R.L.	30	0
60%	None	0	0
	0.2% $NaNO_2$	95 (lt. film)	93 (lt. film)
	N.R.L.	60	20

Table 5

Fingerprint Removal Test

Formulation RIL #245 plus 40% H_2O

Treatment	% Effectiveness of Removal Test (A)	Test (B)
Single Dip	90%	100%
3 Sec. Agitation	95%	100%
5 Sec. Agitation	100%	98-99%
10 Sec. Agitation	85%	98-99%
15 Sec. Agitation	100%	100%
5 Sec. Soak	97%	98-99%
15 Sec. Soak	100%	95%
30 Sec. Soak	100%	99%